



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ :

C23C 16/40

A1

(11) International Publication Number:

WO 00/47797

(43) International Publication Date:

17 August 2000 (17.08.00)

(21) International Application Number: PCT/GB00/00432

(22) International Filing Date: 11 February 2000 (11.02.00)

(30) Priority Data:

9902993.6

11 February 1999 (11.02.99)

GB

(71) Applicant (for all designated States except US): UNIVERSITY OF STRATHCLYDE [GB/GB]; McCance Building, 16 Richmond Street, Glasgow G1 1XQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HITCHMAN, Michael, Leslie [GB/GB]; Flat 2R, 1 Talbot Court, Glasgow G13 3RQ (GB). ZHAO, Junfu [CN/GB]; NIBEC, University of Ulster, Newtownabbey, Co. Antrim BT37 0QB (GB).

(74) Agents: MCCALLUM, William, Potter et al.; Cruikshank & Fairweather, 19 Royal Exchange Square, Glasgow G1 3AE (GB).

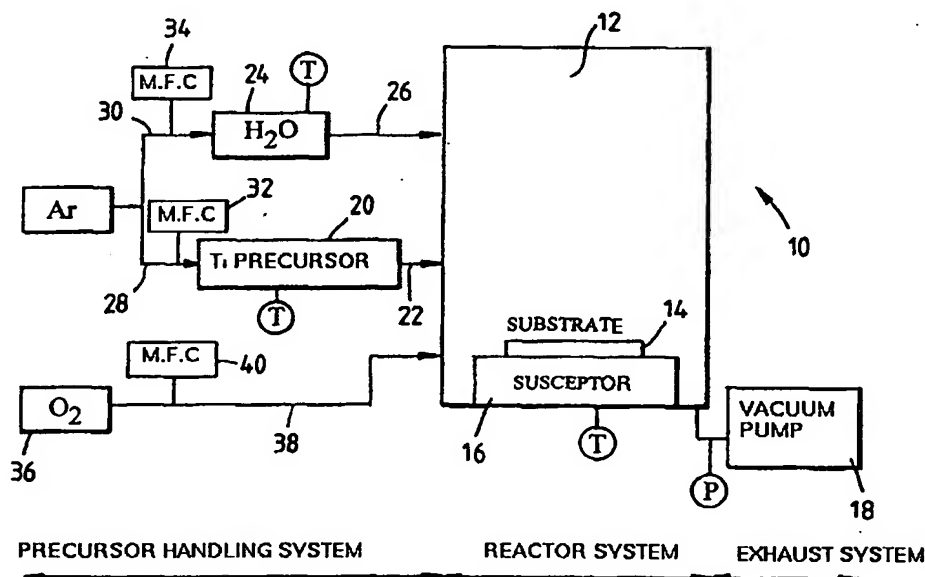
(81) Designated States: JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

(54) Title: LOW PRESSURE CHEMICAL VAPOUR DEPOSITION OF TITANIUM DIOXIDE

- CHEMICAL VAPOUR DEPOSITION



(57) Abstract

A method is provided whereby rutile titanium dioxide may be deposited on a substrate at relatively low temperature; that is, below 500 °C. Titanium dioxide is produced by introduction of a titanium organic precursor compound, such as tertiary titanium tetrabutoxide (TTB), together with oxygen gas and water vapour into a low pressure reaction chamber containing a substrate deposition. Preferred substrates include SnO₂ coated glass, sapphire, silicon, steel or aluminium. Rutile TiO₂ may be deposited using the present method at temperatures as low as 290 °C.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Low Pressure Chemical Vapour Deposition of Titanium Dioxide

5 The present invention relates to a method for depositing rutile titanium dioxide on a substrate by chemical vapour deposition.

10 Titanium dioxide occurs naturally in three crystalline forms: anatase, rutile and brookite. Rutile TiO_2 has excellent anti-reflective properties due to its high refractive index. Rutile is also a useful dielectric and has applications in the microelectronics industry, particularly in the manufacture of memory capacitors.

15 Various techniques have been employed to prepare rutile TiO_2 synthetically. For example, thin films of rutile TiO_2 have been prepared by conventional chemical vapour deposition methods at temperatures in excess of 500°C . Below this temperature, however, titanium dioxide has only been deposited as anatase or in an amorphous state.

20 It is among the objects of the present invention to produce thin films of rutile TiO_2 at temperatures below 500°C .

According to the present invention, there is provided a method for the preparation of rutile TiO_2 , said method comprising:

25 introducing a titanium organic precursor compound, a reactive gas and water vapour into a reaction chamber which is maintained at a reduced pressure; and

30 depositing the titanium dioxide formed as a thin film on a selected substrate at a temperature below 500°C ; wherein said precursor compound substantially comprises tertiary titanium tetrabutoxide. Tertiary titanium tetrabutoxide is also known as titanium tert-butoxide.

Preferably, the temperature is below about 400°C ; and most preferably below about 350°C .

35 Preferably this temperature is also above about 260°C ; preferably also this temperature is above about 290°C . The

substrate may be selected from polycrystalline or single crystalline materials, for example, SnO_2 coated glass, K-glass, steel and aluminium, which materials are polycrystalline, or for example sapphire and silicon, which materials are single crystalline. K-glass is a Registered Trade Mark of Pilkington plc, and refers to glass coated first with a 57nm layer of silica, and then with a 293.5nm layer of SnO_2 . Preferably, substrates such as SnO_2 coated glass, sapphire, silicon, steel or aluminium are used. The surface of the substrate may be heated relative to the walls of the reaction chamber so that decomposition of the precursor and the formation of thin films of TiO_2 is confined to the substrate surface.

In the present method, rutile titanium dioxide is formed at a deposition temperature below 500°C . Preferred deposition temperatures range between 290°C and 400°C . For example, when substrates such as SnO_2 coated glass, sapphire, steel or aluminium are used, the preferred deposition temperature is between 290°C and 322°C . When a substrate such as K-glass is used, the preferred rutile deposition temperature is between 322°C and 400°C .

The precursor may be vaporised prior to being introduced to the reaction chamber. Preferably, the precursor compound is vaporised and introduced into the reaction chamber with a carrier gas. Any inert gas may be used as a carrier; for example, argon or helium. Advantageously, water vapour may also be introduced in the reaction chamber with a carrier gas.

It has been found that the deposition temperature plays a significant role in determining the crystal structure of the titanium dioxide deposited. The rutile phase becomes increasingly dominant as the deposition temperature is increased. For example, an anatase to rutile phase transition is observed at deposition temperatures of approximately 290°C for a titanium dioxide film grown on SnO_2 coated glass. Below that temperature, anatase is the

dominant phase. Above that temperature, rutile becomes increasingly dominant.

The crystal structure of titanium dioxide is also influenced by the nature of the substrate surface. Substrates such as SnO₂, coated glass, sapphire, steel and aluminium exhibit a preference for the rutile phase at deposition temperatures between 290°C and 300°C. When titanium dioxide is deposited on substrates such as K-glass, copper and MgO at similar temperatures, the anatase phase is preferred, although when K-glass is used as a substrate, titanium dioxide begins to be formed as rutile above 322°C. This suggests that the substrate surface plays an important role in the initial nucleation of titanium dioxide films at a given temperature.

In accordance with a second aspect of the present invention, there is provided a substrate having rutile titanium dioxide deposited thereon, in accordance with the method of the first aspect of the present invention.

These and other aspects of the present invention will now be described, by way of example, with reference to the following drawings, in which:

Figure 1 is a block diagram of a system which may be used to prepare rutile TiO₂ in accordance with an embodiment of the method of the present invention;

Figures 2a to 2j are X-ray Diffraction patterns of titanium dioxide films prepared in Example 1,

Figures 3a to 3i show Raman Spectra of titanium dioxide films prepared in Example 1,

Figures 4a to 4h show X-ray Diffraction patterns of titanium dioxide films prepared in Example 2; and

Figures 5a to 5h show Raman Spectra of titanium dioxide films prepared in Example 2.

Reference is first made to Figure 1 which depicts a vertical low pressure chemical vapour deposition system which may be used to deposit titanium dioxide (TiO₂) in the rutile form on a substrate. The system 10 comprises a reaction chamber 12 which contains a heated substrate 14

mounted on a susceptor 16. The reaction chamber 12 is coupled to a vacuum pump 18 which removes gaseous waste products from the reaction chamber 12. The pump also ensures that the pressure in the reaction chamber remains low, at approximately 1.0 Torr.

The system 10 also comprises a vertical bubbler 20 which is coupled to the reaction chamber 12. A titanium organic precursor compound is vaporised in the vertical bubbler 20 and introduced into the reaction chamber through a gas line 22. The gas line 22 is maintained at a temperature above the temperature of the vertical bubbler 20 to prevent the vaporised precursor compound from condensing within the gas line 22.

Also coupled to the reaction chamber 12 is a water bubbler 24. Water is vaporised in the water bubbler 24 and introduced to the upper region of the reaction chamber 12 via a gas line 26. The temperature of the gas line 26 is maintained above the temperature of the water bubbler 24.

The precursor compound and water vapour are introduced into the reaction chamber 12 with a carrier gas of, for example, argon. The carrier gas is fed into the vertical bubbler 20 and water bubbler 24 through inlets 28 and 30, respectively. The rate of flow of carrier gas through the inlets 28 and 30 are controlled independently, by respective mass flow controllers 32, 34.

The reaction chamber 12 is also coupled to a source 36 of oxygen via a gas line 38. The flow of oxygen through the chamber 12 is controlled by a mass flow controller 40.

In operation, the substrate 14 is positioned approximately 3cm from the inlet of the gas line 22 of the vaporised precursor compound. The temperature of the walls of the reaction chamber 12 are maintained at approximately 100°C, so that decomposition of the precursor compound and the formation of titanium dioxide is limited to the heated substrate 14 surface.

In the following examples, the reaction parameters which influence the crystal structure of the deposited

titanium dioxide film are investigated. The films are produced using titanium tetrabutoxide (TTB) (purity >99.95%, InorgTech which has been identified as being comprised substantially of tertiary TTB (also known as titanium tert-butoxide)), as a precursor compound, and electronic grade argon as a carrier gas.

The deposition conditions are summarised in Table 1 below.

Table 1

Deposition conditions	Process parameters
Total Pressure	1.0 Torr
Flow ratio of O ₂ : Ar + H ₂ O: Ar + TTB	3: 2 :1
TTB bubbler temperature	65°C
H ₂ O bath temperature	22 - 23°C

Example 1

In this example, titanium dioxide films are deposited on K-glass, a SnO₂ and silica coated glass substrate at a range of temperatures (Table 2). The samples were analysed to determine the effect of increasing deposition temperature on crystal structure.

Table 2

s	1	2	3	4	5	6	7	8	9
T _d °C	193	215	236	257	268	279	290	300	322

X-ray Diffraction

The crystal structures of the resulting titanium dioxide films were analysed by X-ray Diffraction using Cu-K α radiation at $\lambda=0.15405\text{nm}$ through a 2θ angle of 20° to 100° . All measurements were carried out using a Philips PW

1010 diffractometer operating at 40kV and 20mA with a Ni filter.

The results are shown in Figures 2a to 2j.

Figure 2a is an X-ray Diffraction pattern of the SnO_2 coated K-glass substrate. The polycrystalline SnO_2 coating shows a preferred orientation in the (200) plane, as indicated by the strong characteristic peak at $2\theta = 37.85^\circ$.

Figure 2b shows the X-ray diffraction pattern of Sample 1 ($T_d 193^\circ$). There is no obvious peak which can be identified with a TiO_2 crystal structure.

Figure 2c shows an X-ray diffraction pattern for Sample 2 ($T_d 215^\circ$). Some anatase peaks appear at 2θ angles of 25.4° (101), 37.7° (004), 48.5° (200), 54.95° (211) and 70.15° (220). Substrate peaks, however, are still visible.

The patterns for Samples 3 ($T_d 236^\circ\text{C}$) and 4 ($T_d 257^\circ\text{C}$) are shown in Figures 2d and 2e, respectively. Anatase peaks are observed in both samples, at 2θ angles of 25.3° (101), 37.75° (004), 48.0° (200), 54.9° (211) and 70.2° (220) for Sample 3; and 25.5° (101), 37.9° (004), 48.1° (200), 55.15° (211) and 70.25° (220) for Sample 4. The relative intensities of these diffraction peaks differ from those reported in the literature. This suggests that the deposited anatase phase is polycrystalline with randomly oriented grains.

Figure 2f is an X-ray pattern for Sample 5 ($T_d 268^\circ\text{C}$). Titanium dioxide is deposited as a mixture of anatase and rutile, but the anatase phase is dominant with peaks arising from the (101), (004), (200), (211) and (210) anatase planes. A strong rutile peak is observed at $2\theta = 39.4^\circ$, assigned to the (200) plane. Other weak rutile peaks are observed at $2\theta = 44.3^\circ$ (210), 62.5° (002), 65.1° (221), 82.3° (321), 85.45° (400), and 95.85° (312).

A significant change is observed with the pattern for Sample 6 ($T_d 279^\circ\text{C}$) (Figure 2g). Only two weak anatase peaks are observed at 37.85° (004) and 55.0° (221). The strong peaks at 2θ values of 39.25° and 64.0° arise from the (200) and (310) rutile planes. Other rutile peaks are observed at $2\theta = 36.25^\circ$ (101), 44.1° (210) and 84.55° (400).

Figure 2h shows a pattern for Sample 7 ($T_d 290^\circ\text{C}$). The

rutile phase appears to be increasingly dominant as the temperature is increased.

Figures 2i and 2j are X-ray patterns for titanium dioxide films formed at 300°C and 322°C, respectively. The patterns show that the rutile phase is dominant, with strong peaks arising from 2θ values of 36.3° (101), 39.4° (200) and 84.4° (400) for Sample 8; and at 2θ values of 36.15° (101), 39.3° (200) and 84.4° (400) for Sample 9.

These results show conclusively that rutile may be prepared by low pressure chemical deposition at temperatures below 500°C. In particular, the samples prepared above 300°C (Samples 8 and 9) are composed exclusively of the rutile phase.

Raman Spectroscopy

The crystal structures of Samples 1 to 9 were also analysed by Raman Spectroscopy. All measurements were carried out using a 514.5nm argon laser produced by a Renishaw Raman Spectrometer.

Literature values for lattice vibrations of the anatase phase are 194 cm⁻¹, 397 cm⁻¹, 515 cm⁻¹ and 637 cm⁻¹. Typical rutile vibrations occur at 144 cm⁻¹, 235 cm⁻¹, 448 cm⁻¹ and 612 cm⁻¹.

The Raman spectra for Samples 1 to 9 are shown in Figures 3a to 3i.

Figure 3a shows that no crystalline structure peaks can be detected by Raman scattering for a film deposited at 193°C. At a deposition temperature of 215°C (Figure 3b), two peaks are observed at 514 cm⁻¹ and 640 cm⁻¹. These correspond to the anatase phase.

Figures 3c and 3d show Raman spectra for Samples 3 and 4, prepared at deposition temperatures of 236 and 257°C, respectively. Peaks at 392 cm⁻¹, 514 cm⁻¹ and 637 cm⁻¹, corresponding to the anatase phase are observed.

Samples 5 and 6, prepared at 268°C and 279°C, respectively, are composed of a mixture of the anatase and rutile phase. As shown in Figures 3e and 3f, anatase peaks are observed at 395 cm⁻¹ and 635 cm⁻¹, and rutile peaks are

observed at 441 cm^{-1} and 519 cm^{-1} .

At deposition temperatures of 290°C (Sample 7), rutile peaks are observed at 448cm^{-1} and 607cm^{-1} . The peaks increase in intensity as the deposition temperature increases. Samples 8 and 9, prepared at deposition temperatures of 300°C and 322°C , respectively, show two strong rutile vibrations at 445 cm^{-1} and 610 cm^{-1} . A very weak anatase vibration is also observed at 519 cm^{-1} .

The results of the Raman analysis are consistent with the results obtained by X-ray diffraction.

Example 2

In this example, titanium dioxide is deposited on a range of substrates to determine how the nature of the substrate affects the crystal structure of the titanium dioxide formed.

The titanium dioxide films analysed in this example are listed in Table 3 below.

Table 3

Sample	Substrate	Td ($^{\circ}\text{C}$)
10	glass	268
11	glass	290
12	glass	305
13	glass	322
14	sapphire	300
15	steel	298
16	aluminium	298
17	magnesium oxide	298

X-ray Diffraction

The crystal structures of the Samples 10 to 17 were analysed using the diffractometer of Example 1. The resulting patterns of the samples are shown in Figures 4a to 4h.

The bottom trace of Figure 4a shows an X-ray diffraction pattern for K-glass. Unlike SnO₂ coated glass, K-glass is unoriented and no characteristic peaks are observed. The top trace of Figure 4a shows an X-ray diffraction pattern for titanium dioxide deposited on glass at 268°C (Sample 10). The peaks arise from the anatase (101) (200) (211) and (220) planes. Weak signals corresponding to the (112) (312) and (321) planes are also observed.

The effect of changing the substrate from SnO₂ coated glass to K-glass can be seen by comparing the pattern of Figure 2f with the top trace of Figure 4a. The strong anatase (004) peak in Figure 2f is replaced by a weak peak corresponding to the anatase (112) plane. A further difference is that no rutile peaks are observed when titanium dioxide is deposited on K-glass at 268°C.

The anatase phase remains the dominant phase at deposition temperatures of 290° (Sample 11, Figure 4b) and 305°C (Sample 12, Figure 4c). As the deposition temperature is increased to 322°C in Sample 13, however, rutile peaks are observed at 2θ angles of 27.2° (110), 39.3° (200), 41.7° (111) and 84.2° (400) (Figure 4d).

The results indicate that higher deposition temperatures are required to deposit rutile on un-oriented glass than on oriented SnO₂-coated glass.

Figure 4e is an X-ray diffraction pattern for titanium dioxide deposited on a sapphire substrate at 300°C (Sample 14). The pattern shows strong rutile peaks at 2θ values of 39.25° (200) and 84.2° (400). Other weak rutile signals are observed at 36.05° (101), 41.3° (111) and 54.35° (211). A broad rutile (110) peak is observed at 27.6°.

Figure 4f compares an X-ray diffraction pattern of a steel substrate (bottom trace) with an X-ray pattern for Sample 15 (top trace). The sample is prepared using a steel substrate at a deposition temperature of 298°C. Titanium dioxide is deposited as rutile and a strong rutile peak is observed at 39.0° (200). A signal from either the steel

substrate or from a rutile phase is also observed at 44.0° .

Figure 4g compares an X-ray pattern for aluminium (bottom trace) with an X-ray pattern for titanium dioxide deposited on aluminium at 298°C (Sample 16). Rutile appears to be the dominant phase, with peaks appearing at 2θ values of $36.25^\circ(101)$, $39.3^\circ(200)$, $65.25^\circ(221)$ and $48.1^\circ(400)$.

Figure 4h shows an X-ray pattern of titanium dioxide deposited on magnesium oxide at a deposition temperature of 298° . The spectrum shows anatase peaks at 2θ values of $47.9^\circ(200)$, $54.95^\circ(211)$, $70.1^\circ(220)$ and $95.05^\circ(321)$. Anatase is the dominant phase in this sample. However, the rutile phase is also present and a rutile peak at $27.2^\circ(110)$ is observed.

Raman Spectroscopy

The crystal structures of samples 10, and 12 to 17 were also analysed by Raman Spectroscopy. The resulting spectra are shown in Figures 5a to g. Figure 5h is a Raman spectrum of a sample prepared using a copper substrate at a deposition temperature of 294°C .

Figures 5a to c show Raman spectra for films deposited on glass at 268°C , 305°C and 322°C , respectively. It is clear from Figures 5a and 5b that titanium dioxide is deposited as anatase at temperatures of 268°C and 305°C (Samples 10 and 12). At 322°C (Sample 13, Figure 5c), however, titanium dioxide is deposited as a mixture of mainly rutile with some anatase.

Figure 5d shows a Raman spectrum of titanium dioxide deposited on sapphire at 294°C , rather than the 300°C of sample 14 (Figure 4e). A pure rutile phase is observed with characteristic vibrations at 449cm^{-1} , 515cm^{-1} and 607cm^{-1} .

Figures 5e and 5f show Raman spectra for films deposited on steel and aluminium respectively. Rutile is the dominant phase.

Figures 5g and 5h show Raman spectra for films deposited on MgO and copper respectively. The anatase phase is dominant.

These results indicate that the nature of the

substrate has a significant effect on the crystal structure of the titanium dioxide films. When titanium dioxide is deposited at approximately 290°C to 300°C on substrates such as SnO₂ coated glass, sapphire, steel and aluminium, the rutile phase is dominant. In contrast, when titanium dioxide is deposited on glass, copper and MgO at similar temperatures, the anatase phase is preferred. Also, a phase transition from anatase to rutile is observed at 290°C for a film grown on SnO₂ coated glass. In contrast, when glass is used as a substrate, the same phase transition occurs at 322°C. This suggests that the substrate surface plays an important role in the initial nucleation of titanium dioxide films at a given temperature.

Conclusions from Examples 1 and 2

The Examples above show that reaction conditions have a significant effect on the crystal structure of titanium dioxide formed by LPCVD of TTB at 1.0 Torr.

By depositing titanium dioxide on a substrate of SnO₂ coated glass at temperatures in the range of 290°C and 322°C, a rutile titanium dioxide film is formed with preferred orientations of (200) and (400). At deposition temperatures between 236°C and 257°C, an anatase film of titanium dioxide is formed with oriented faces of (101) (112) (200), (211) and (220). At 268°C, a mixture of rutile and anatase is formed.

At deposition temperatures between 215°C to 236°C titanium dioxide deposited on SnO₂ coated glass undergoes an amorphous to anatase phase transition. At deposition temperatures between 257°C and 290°C, an anatase to rutile transition is observed.

The nature of the substrate also has a significant effect on the crystal structure of the titanium dioxide films. The orientations of the films depend on the orientations of the substrate surface. Rutile TiO₂ films can be selectively formed on SnO₂ coated glass, sapphire, steel and aluminium substrates at deposition temperatures of approximately 300°C.

12

and aluminium substrates at deposition temperatures of approximately 300°C.

5

10

15

20

25

30

35

CLAIMS

1. A method for the preparation of rutile TiO_2 , the method comprising:

5 introducing a titanium organic precursor compound, a reactive gas and water vapour into a reaction chamber which is maintained at a reduced pressure; and

 depositing the titanium dioxide formed as a thin film on a selected substrate at a temperature below 500°C ;

10 wherein said precursor compound substantially comprises tertiary titanium tetrabutoxide.

2. The method of claim 1 wherein said temperature is below about 400°C .

15 3. The method of claim 2 wherein said temperature is below about 350°C .

20 4. The method of any preceding claim wherein said temperature is above about 260°C .

 5. The method of claim 4 wherein said temperature is above 290°C .

25 6. The method of any preceding claim wherein said substrate is a polycrystalline material.

30 7. The method of claim 6 wherein said substrate is selected from: SnO_2 , coated glass, K-glass, steel, and aluminium.

 8. The method of any of claims 1 to 5 wherein said substrate is a single crystalline material.

35 9. The method of claim 8 wherein said substrate is selected from: sapphire or silicon.

10. The method of any preceding claim wherein the surface of said substrate is heated relative to the reaction chamber.

5 11. The method of any preceding claim wherein said precursor is vaporised prior to being introduced into the reaction chamber.

10 12. The method of claim 11 wherein said vaporised precursor is introduced into the reaction chamber with a carrier gas.

15 13. The method of claim 12 wherein said carrier gas is an inert gas.

14. The method of claim 13 wherein said carrier gas comprises argon or helium.

20 15. The method of any preceding claim wherein the water vapour is introduced into the reaction chamber with a carrier gas.

25 16. The method of any preceding claim wherein the reaction chamber is maintained at a pressure of around 1 Torr.

17. The method of any preceding claim wherein the reactive gas comprises oxygen.

30 18. A substrate having a thin film of titanium dioxide in its rutile form deposited thereon in accordance with the method of claim 1.

1/14

- Chemical Vapour Deposition

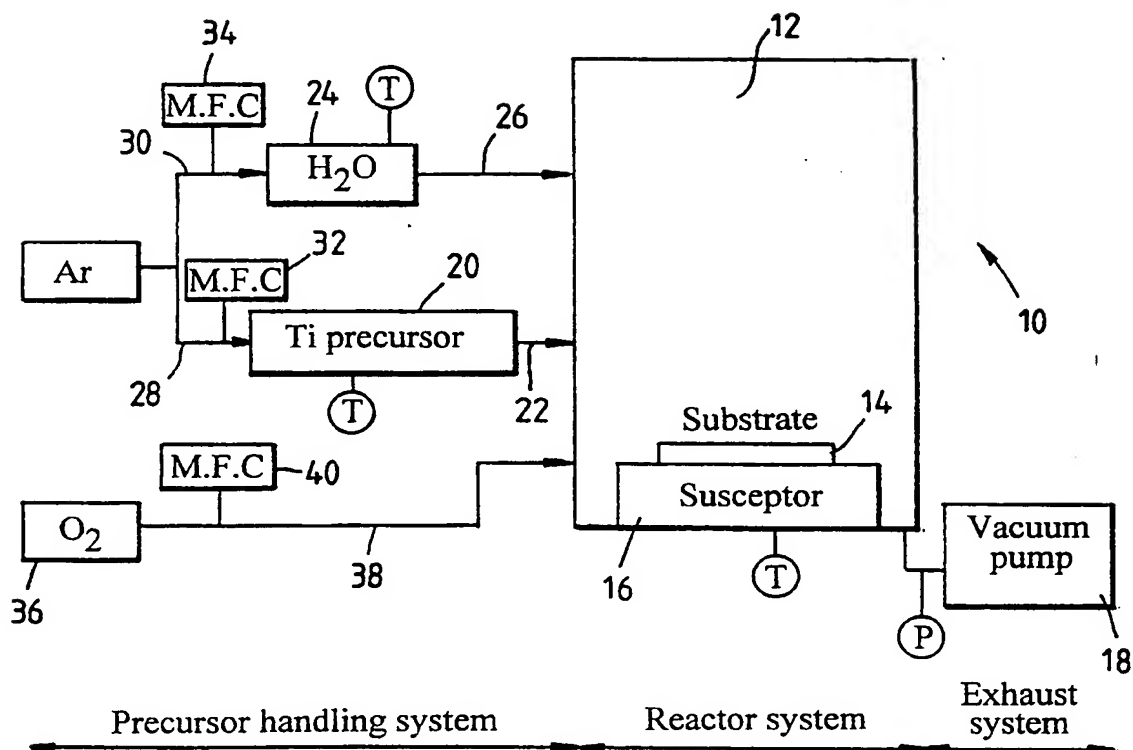


Fig. 1

2/14

Effect of deposition temperatures on the crystalline structures of TiO_2 thin films by x-ray diffraction measurement (a-anatase, r-rutile, s-substrate)

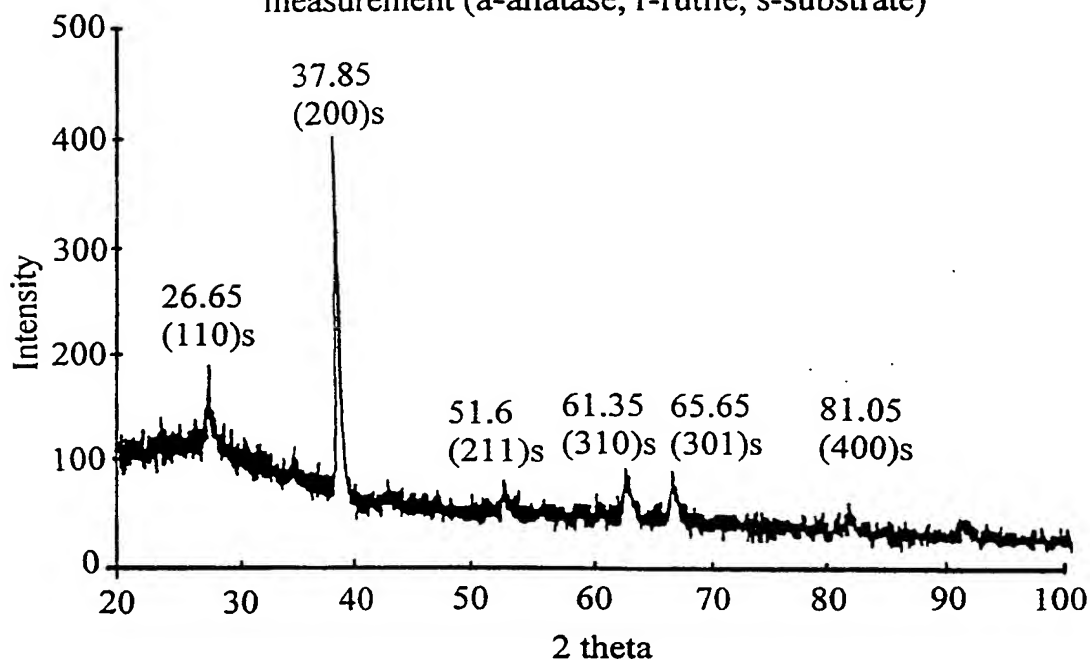


Fig. 2a

Background of SnO_2 coated K-glass

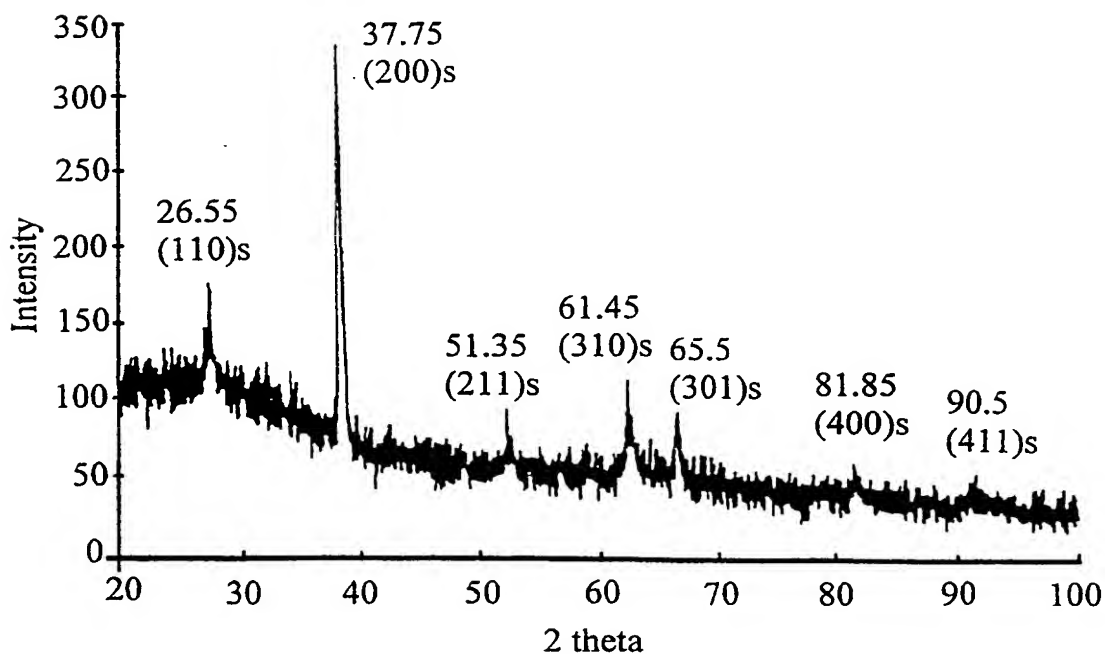


Fig. 2b

TiO_2 films on SnO_2 coated K-glass T_d -193°C

3/14

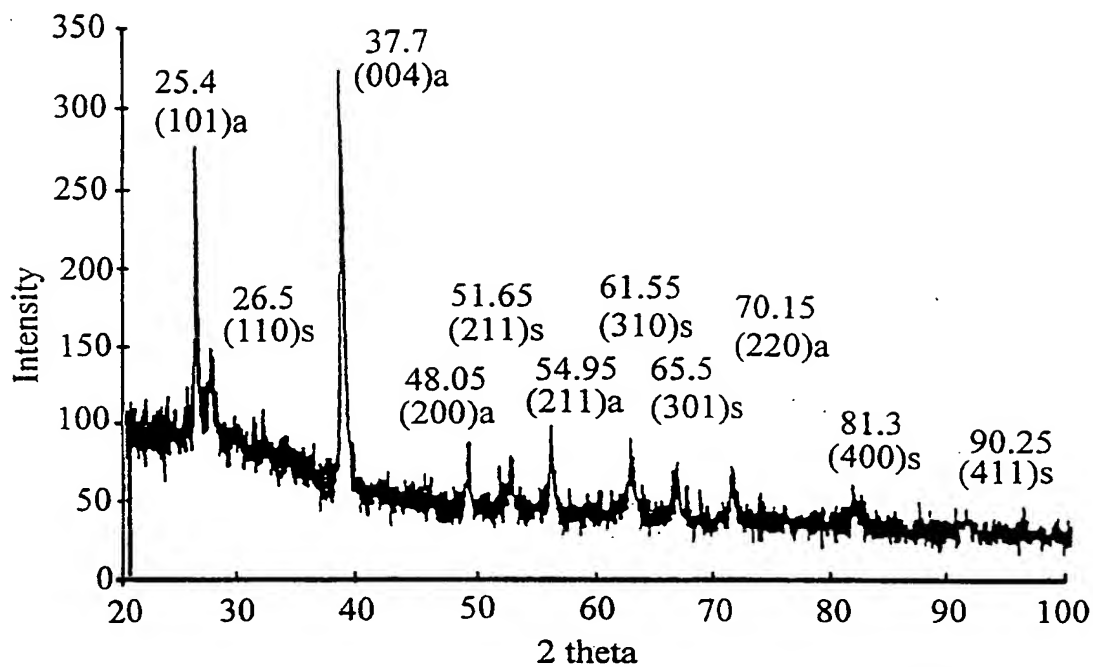
TiO₂ films on SnO₂ coated K-glass T_d-215°C

Fig. 2c

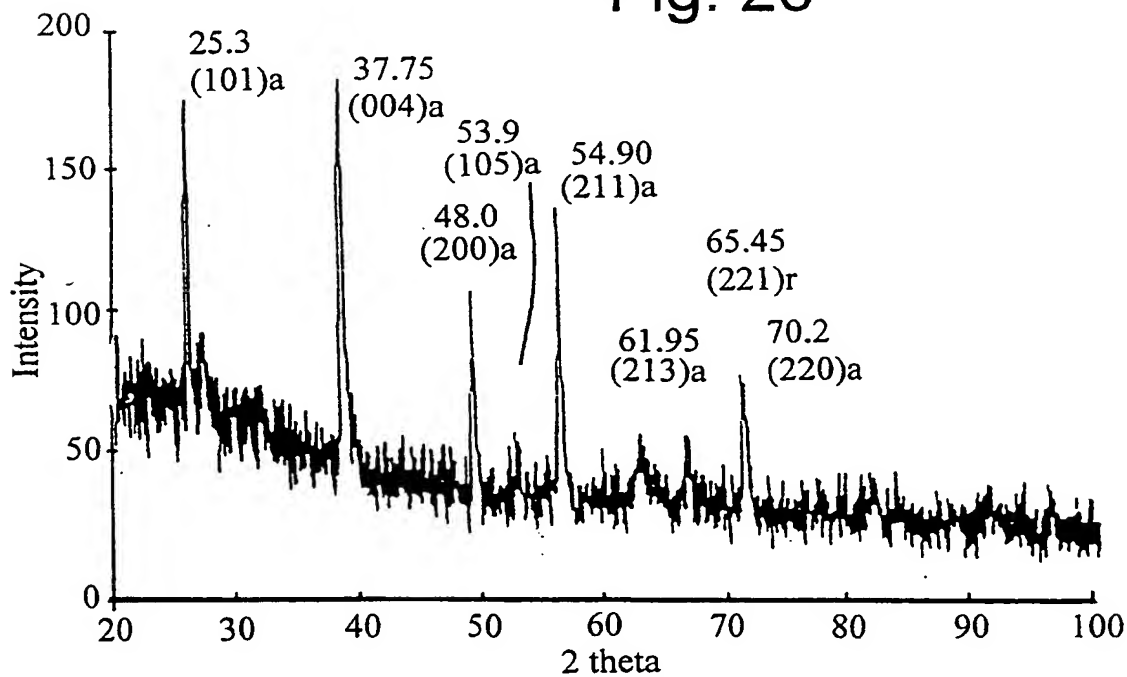
TiO₂ films on SnO₂ coated K-glass T_d-236°C

Fig. 2d

4/14

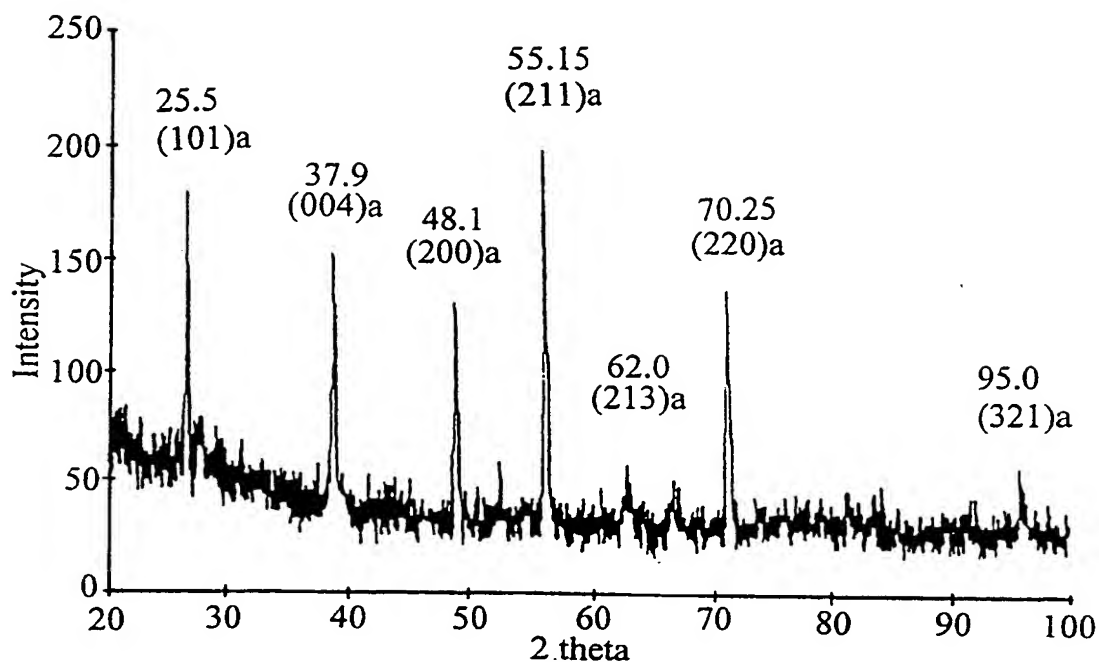
TiO₂ films on SnO₂ coated K-glass T_d-257°C

Fig. 2e

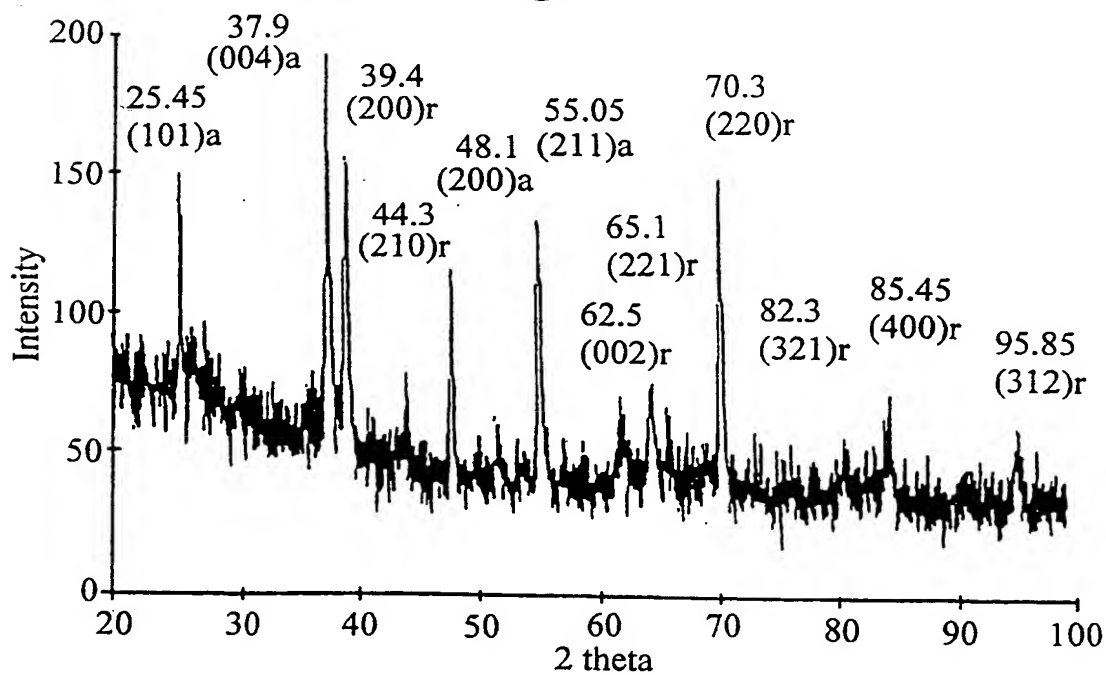
TiO₂ films on SnO₂ coated K-glass T_d-268°C

Fig. 2f

5/14

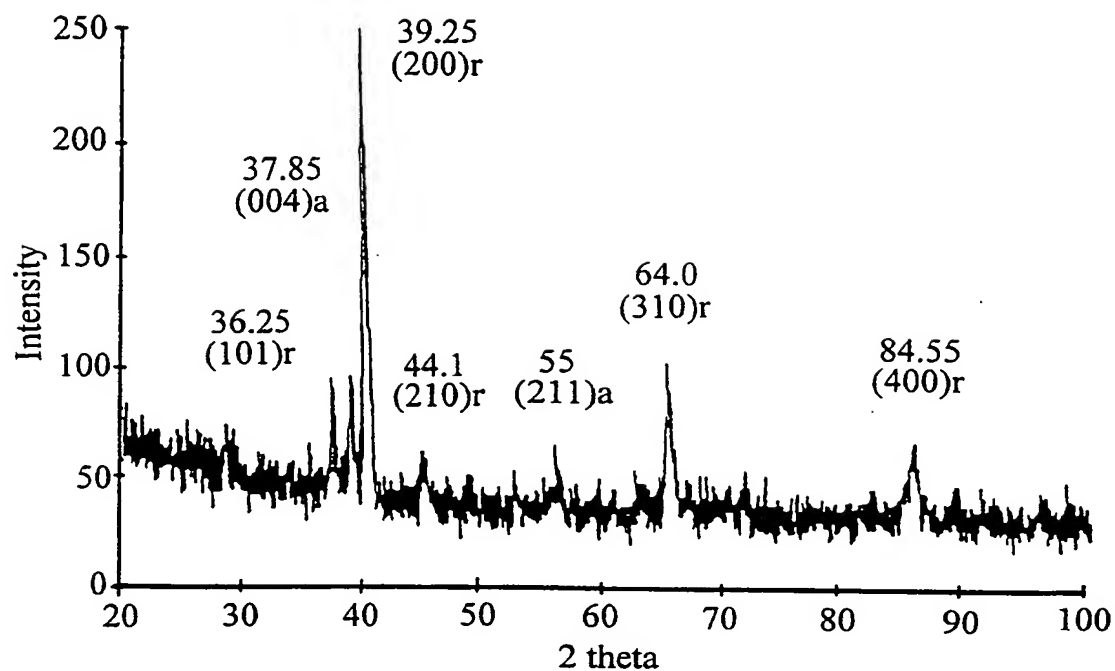
TiO₂ films on SnO₂ coated K-glass T_d-279°C

Fig. 2g

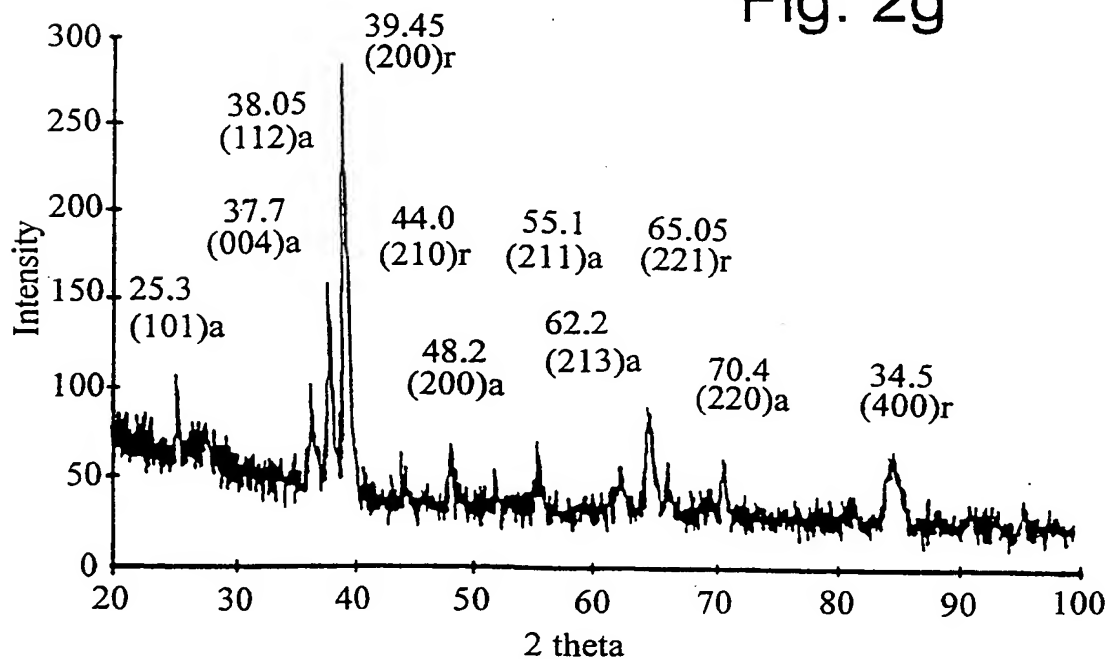
TiO₂ films on SnO₂ coated K-glass T_d-290°C

Fig. 2h

6/14

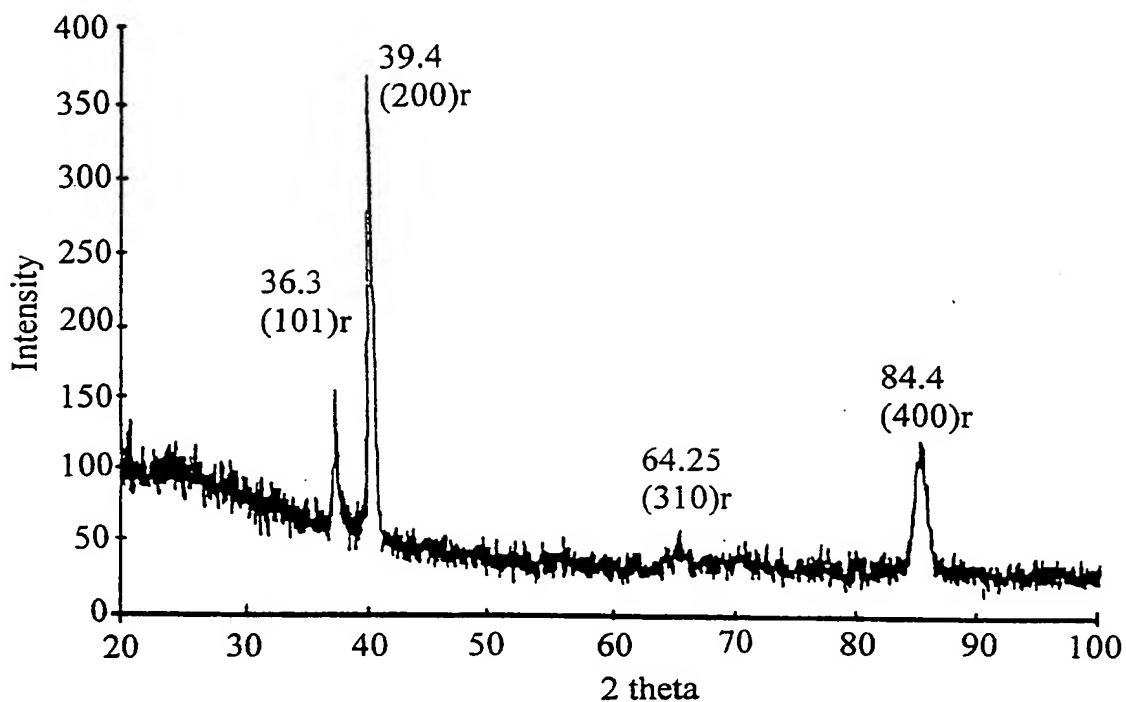
TiO₂ films on SnO₂ coated K-glass T_d-300°C

Fig. 2i

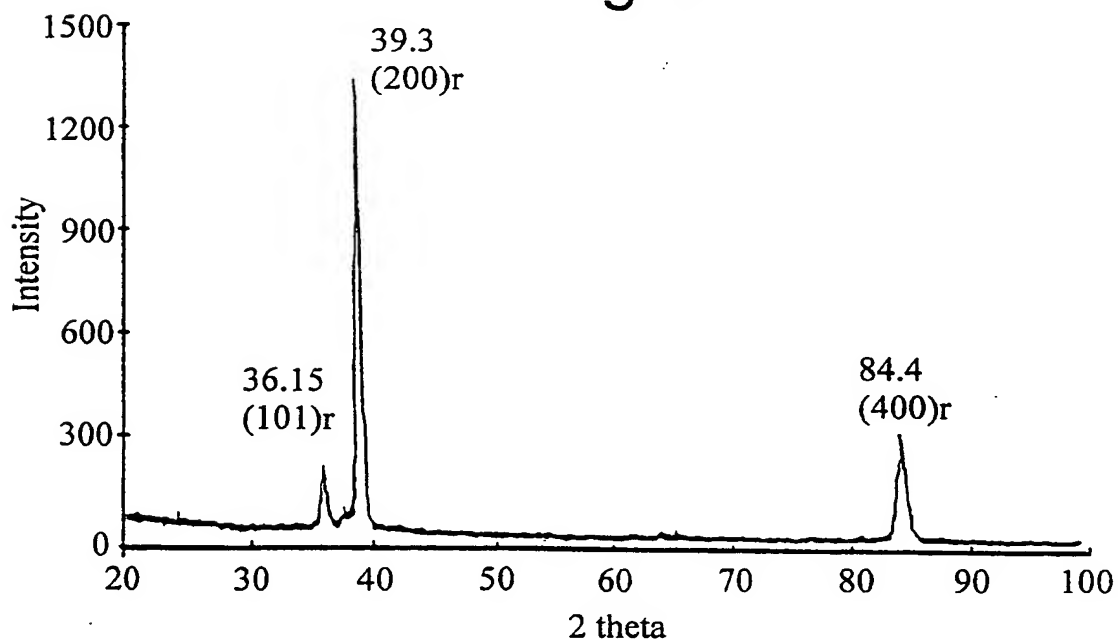
TiO₂ films on SnO₂ coated K-glass T_d-322°C

Fig. 2j

7/14

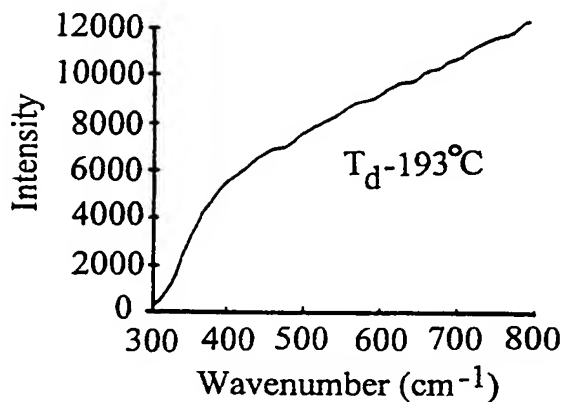
Raman spectra of TiO₂ films at different temperatures

Fig. 3a

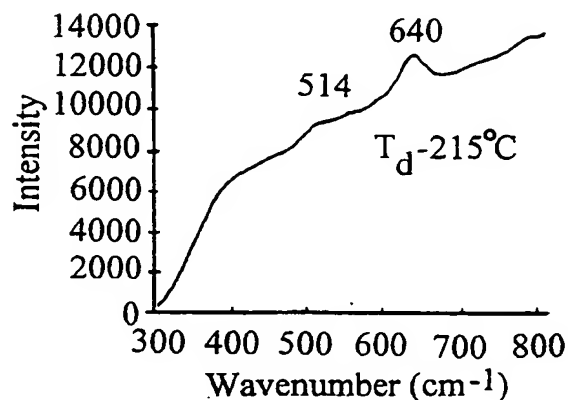


Fig. 3b

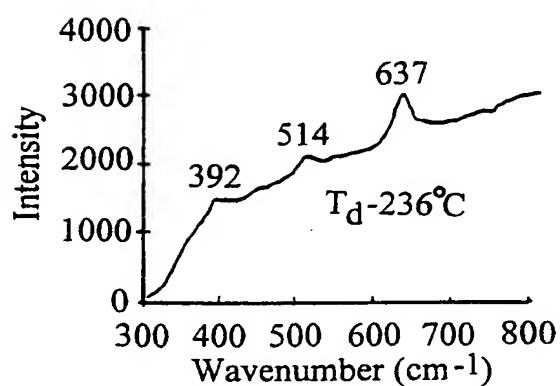


Fig. 3c

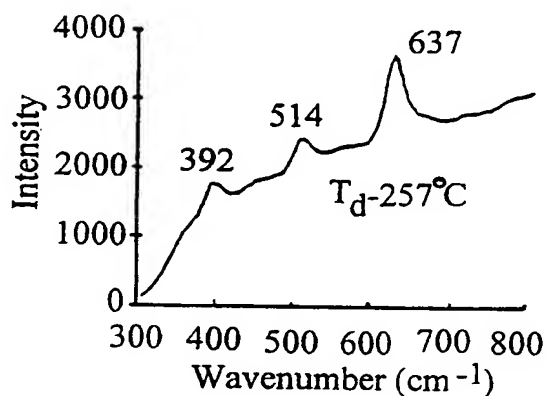


Fig. 3d

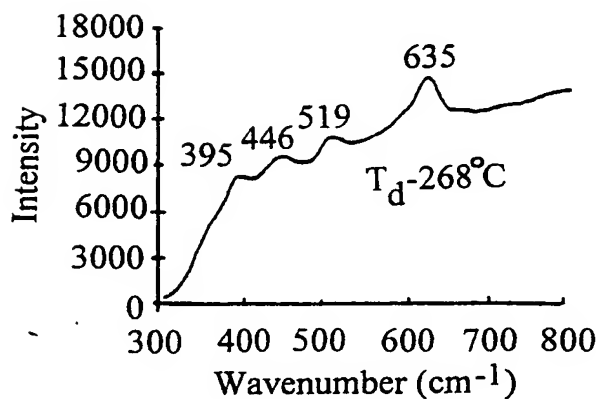


Fig. 3e

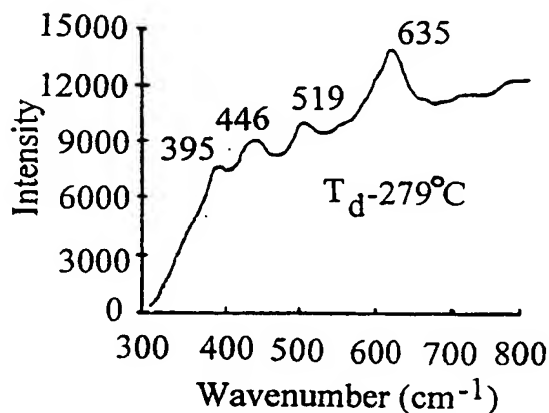


Fig. 3f

8/14

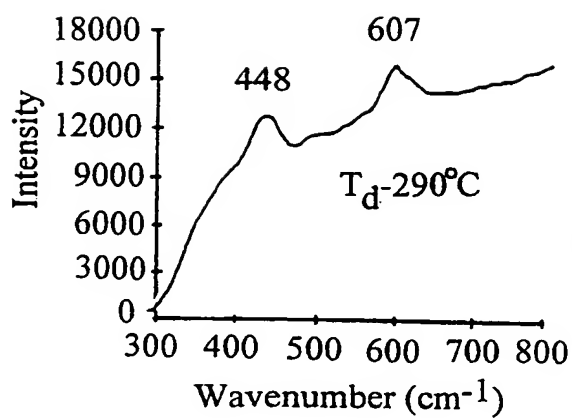


Fig. 3g

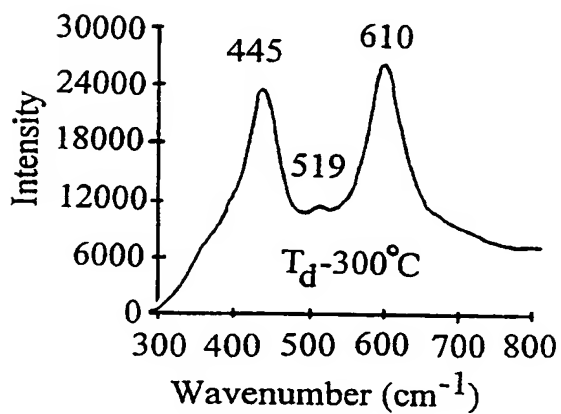


Fig. 3h

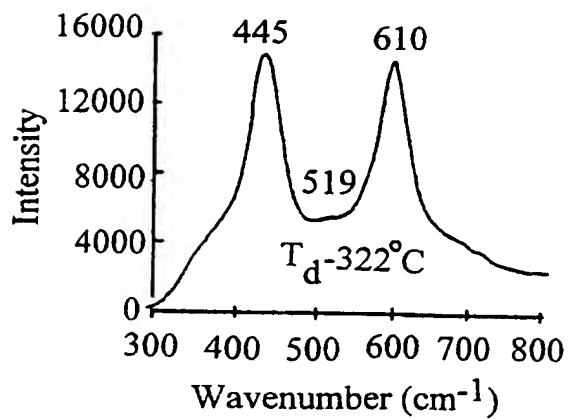
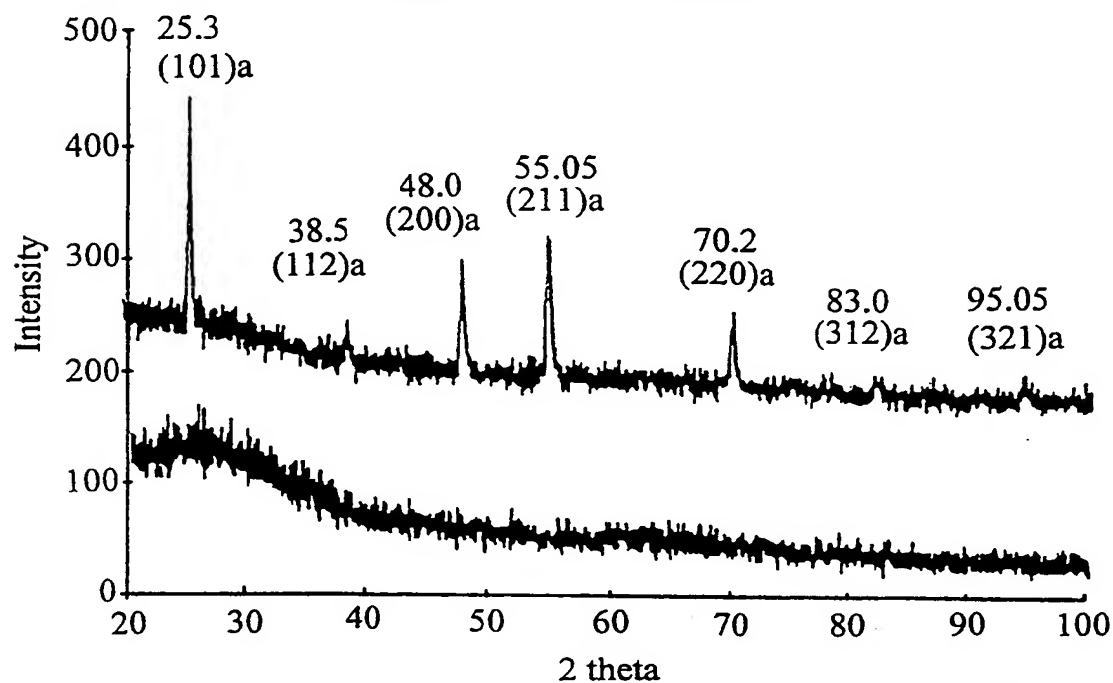


Fig. 3i

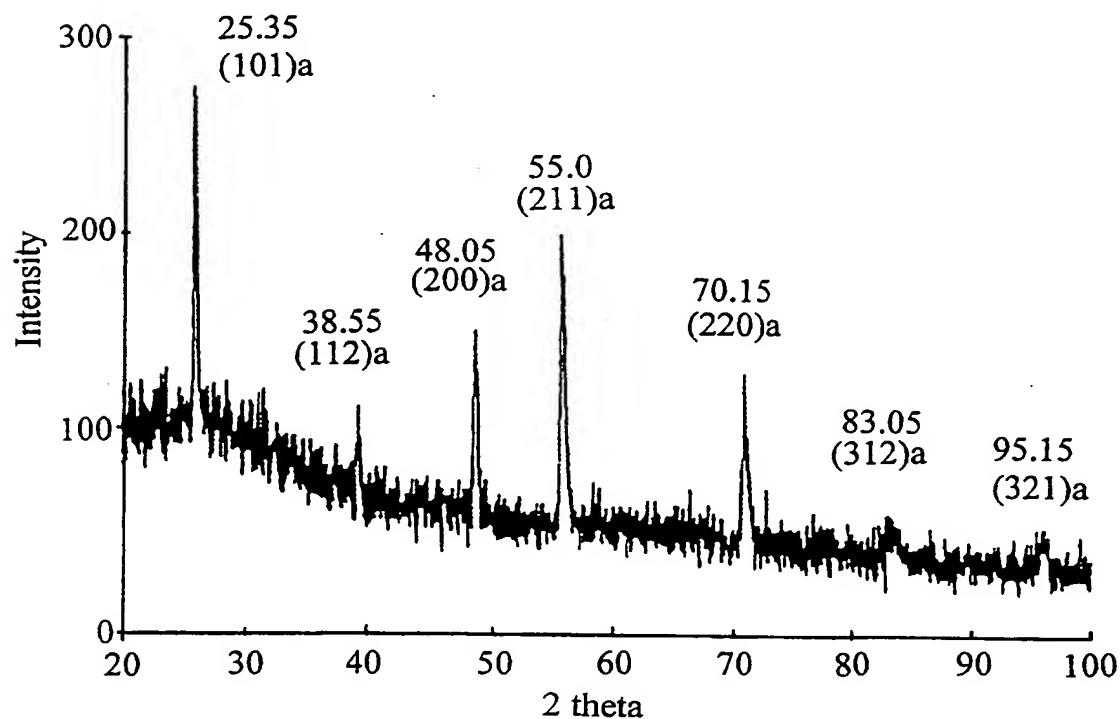
9/14

Effect of substrates and temperatures on the crystalline structures
of TiO₂ films (a-anatase, r-rutile, s-substrate)



TiO₂ films on glass. T_d-268°C (top line)
x-ray spectrum of glass (bottom line)

Fig. 4a



TiO₂ films on glass. T_d-290°C
SUBSTITUTE SHEET (RULE 26)

Fig. 4b

10/14

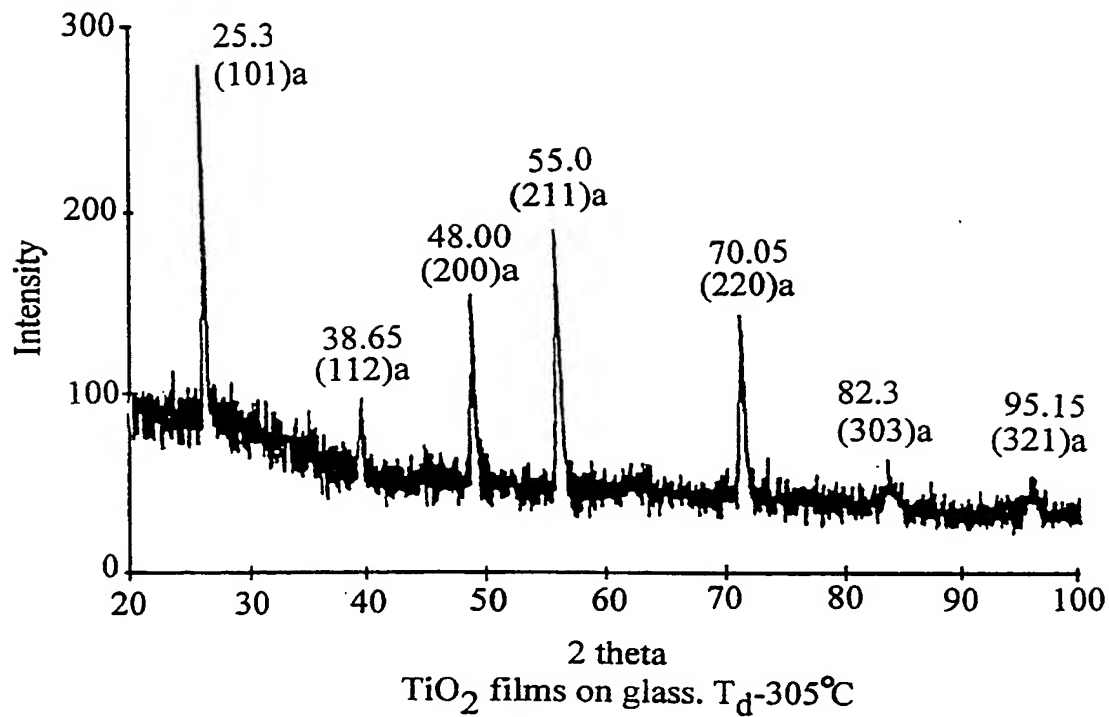


Fig. 4c

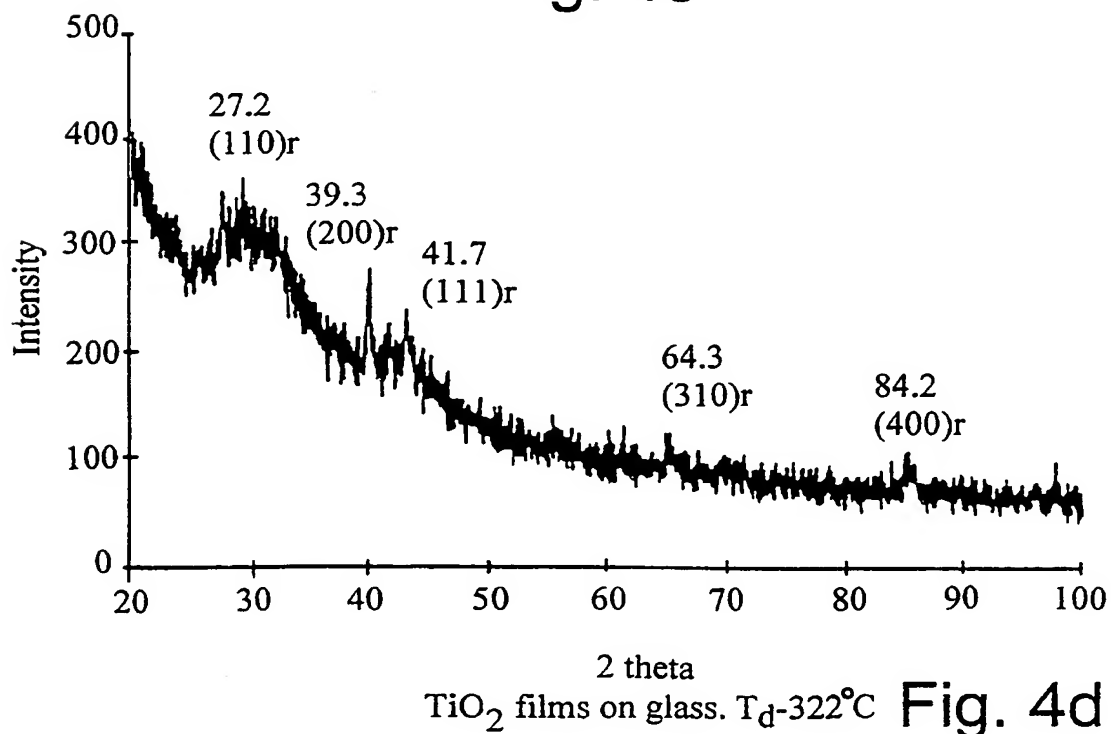


Fig. 4d

11/14

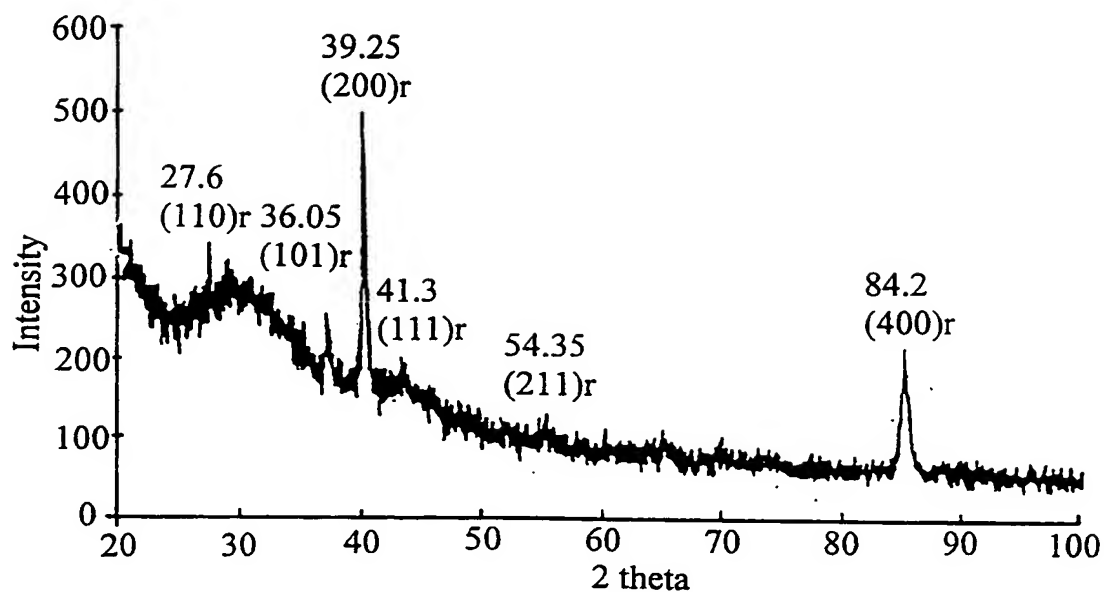
TiO₂ films on sapphire substrate. T_d-300 C

Fig. 4e

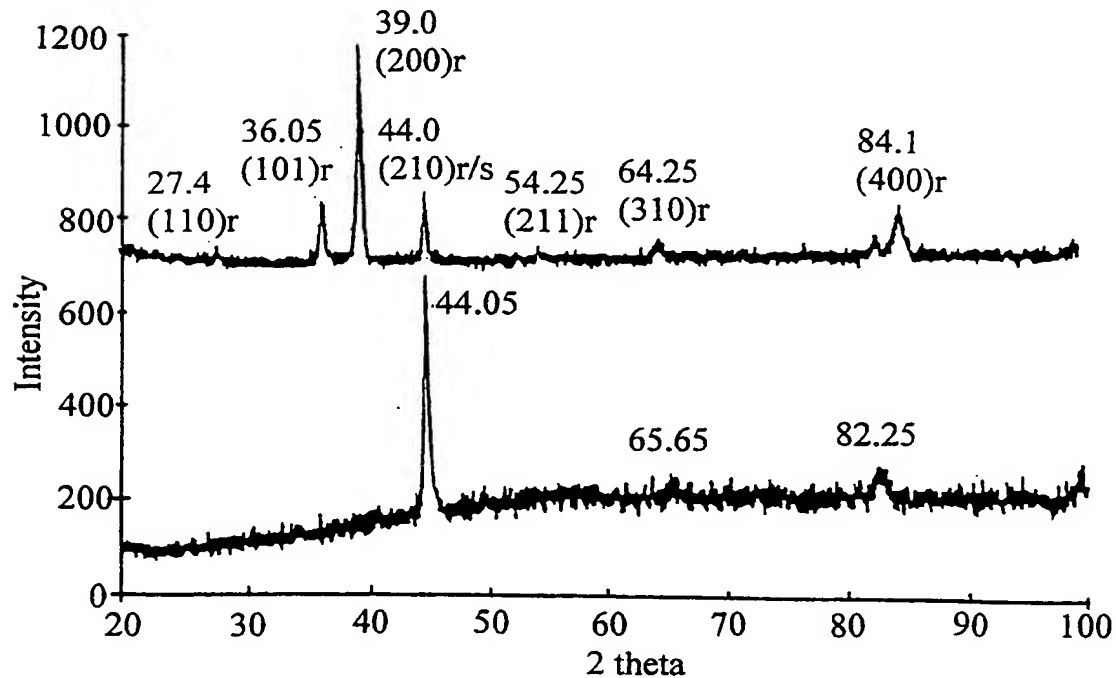
TiO₂ films on steel plate (top curve).
T_d-298 C XRD of steel (bottom curve)

Fig. 4f

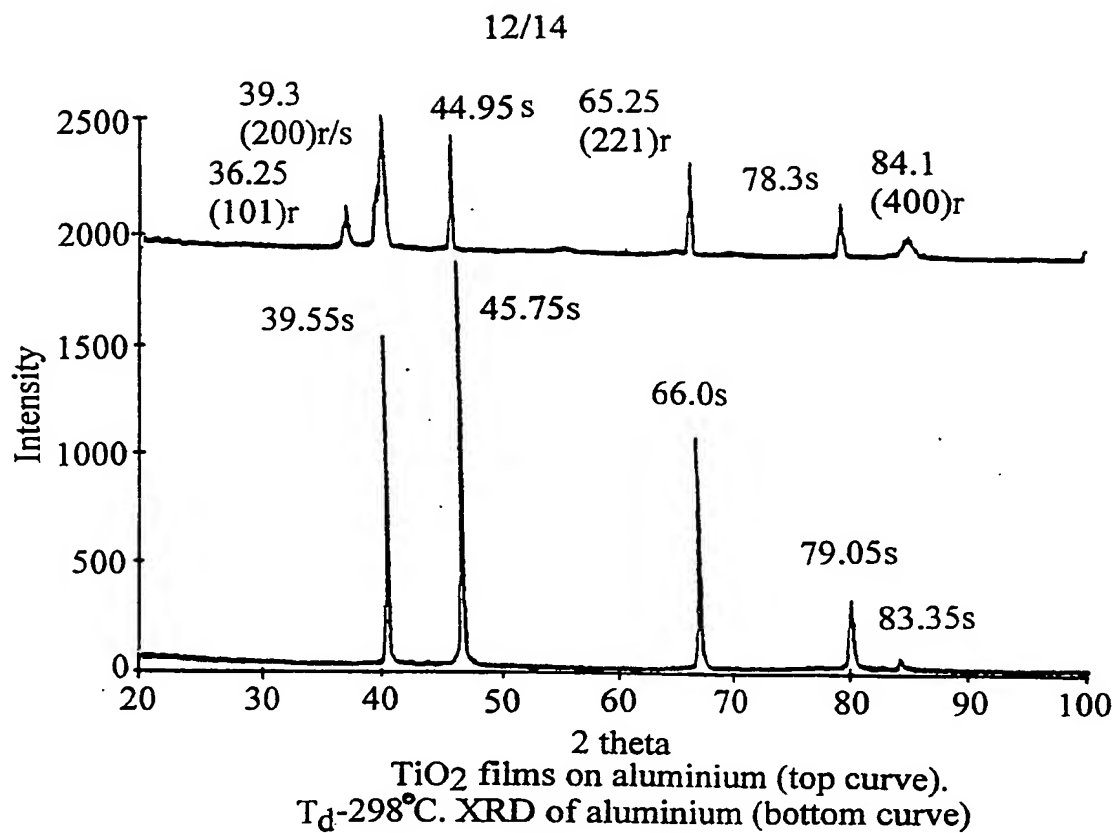


Fig. 4g

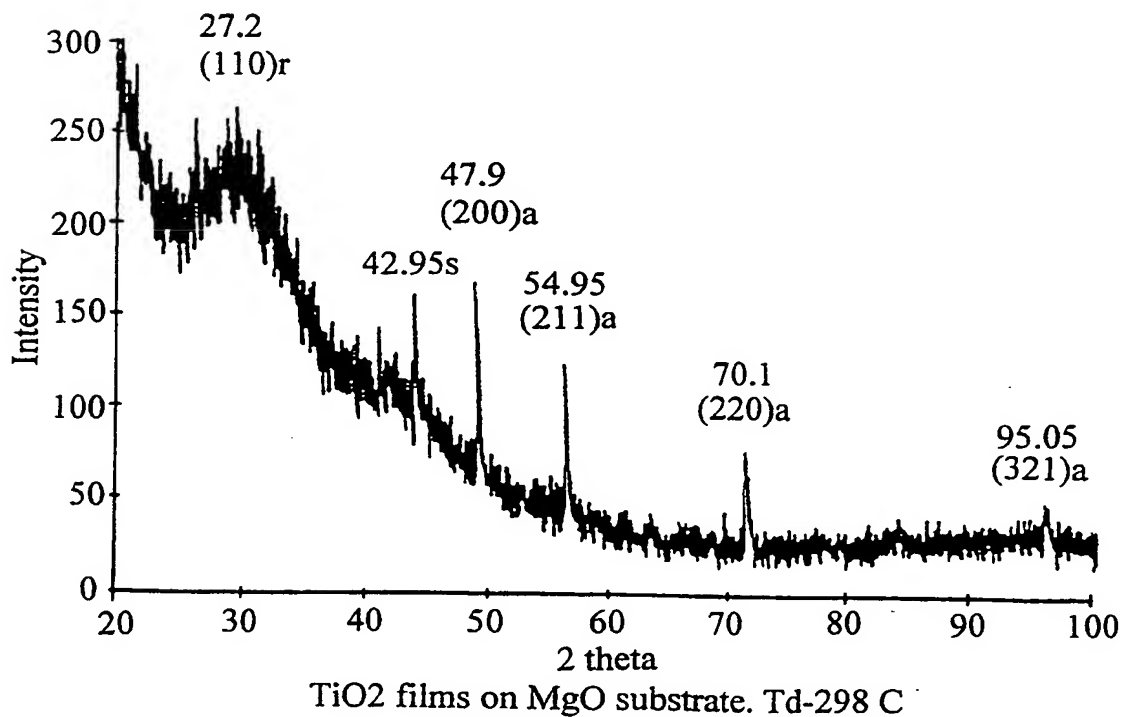


Fig. 4h

13/14

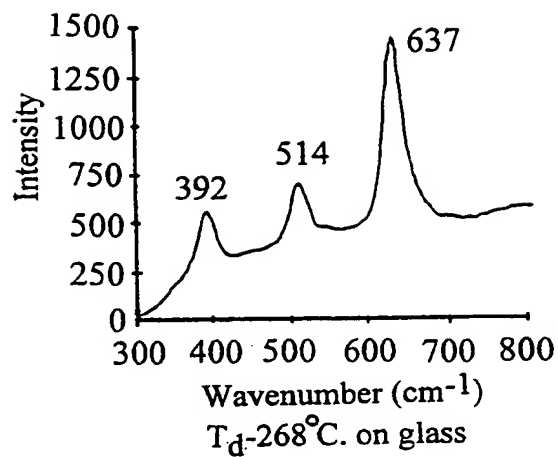


Fig. 5a

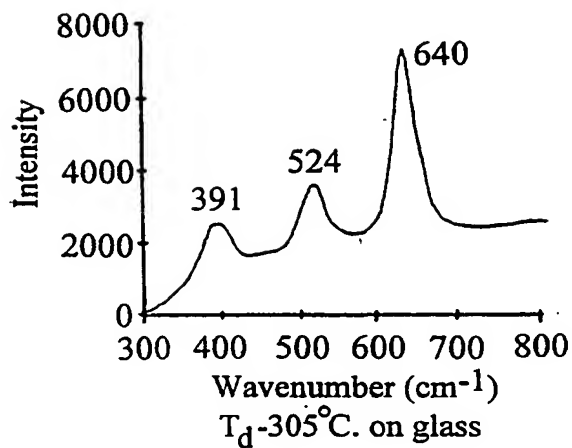


Fig. 5b

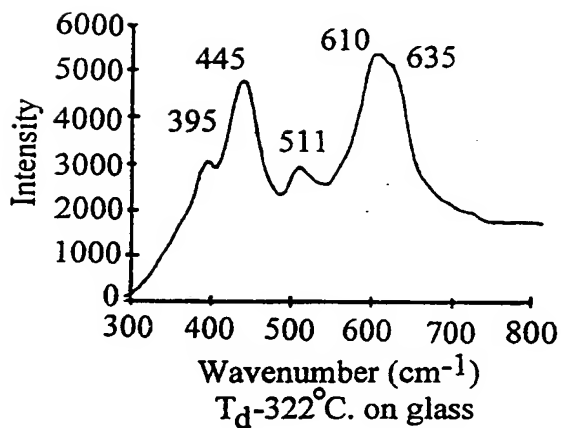


Fig. 5c

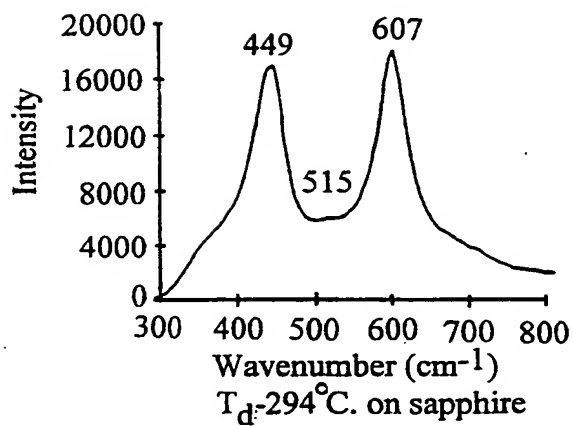


Fig. 5d

14/14

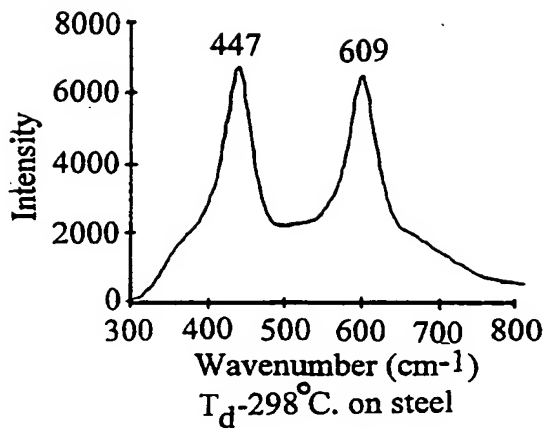


Fig. 5e

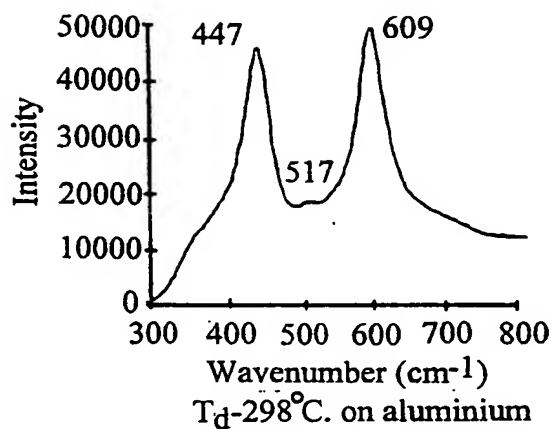


Fig. 5f

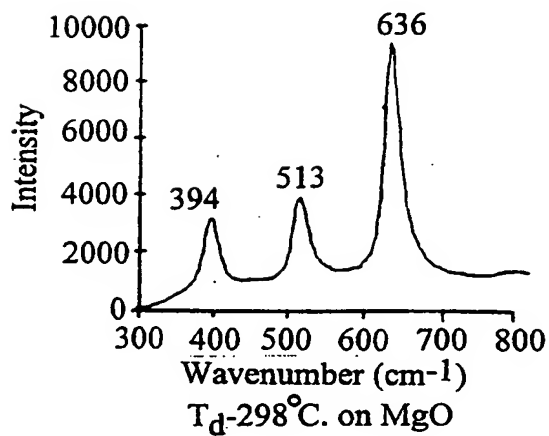


Fig. 5g

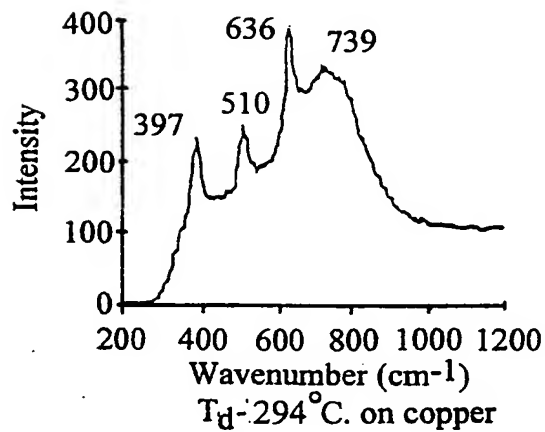


Fig. 5h

INTERNATIONAL SEARCH REPORT

In International Application No

PCT/IB 00/00432

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C16/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KIM E K ET AL: "Growth of highly oriented TiO2 thin films on InP(100) substrates by metalorganic chemical vapor deposition" JOURNAL OF CRYSTAL GROWTH, NL, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, vol. 170, no. 1-4, 1 January 1997 (1997-01-01), pages 803-807, XP004087222 ISSN: 0022-0248	18
A	the whole document — —/—	1-17

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

16 May 2000

Date of mailing of the international search report

29/05/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ekhuft, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00432

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 119, no. 20, 15 November 1993 (1993-11-15) Columbus, Ohio, US; abstract no. 208940, HU, LIMING ET AL: "Form control of ultrafine particles in the chemical vapor deposition reactor. I. Preparation of titania ultrafine particles" XP002136989 abstract -& HUADONG HUAGONG XUEYUAN XUEBAO (1992), 18(4), 417-22, 1 PLATE, 1992, XP000909254 figure 1	1-17
A	CHEMICAL ABSTRACTS, PHYSICAL AND ANALYTICAL CHEMISTRY SECTIONS, vol. 74, no. 12, 22 March 1971 (1971-03-22), page 515 XP002136988 US *ABSTRACT No. 58305x*	1-17
A	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB TOLSTIKHINA A L ET AL: "Specific features of the structure of amorphous titanium dioxide films synthesized under various conditions" Database accession no. 5269755 XP002137839 abstract -& KRISTALLOGRAFIYA, MARCH-APRIL 1996, MAIK NAUKA/INTERPERIODICA PUBLISHING, RUSSIA, vol. 41, no. 2, pages 339-347, XP000909002 ISSN: 0023-4761	1-17